

1 LOW CONDUCTIVITY AND SINTERING-RESISTANT THERMAL BARRIER
2 COATINGS
3

4 CROSS-REFERENCE TO RELATED APPLICATIONS

5 *INS A* > This application claims the benefit of U.S. Provisional
6 Patent Application Serial No. 60/263,257 filed January 22, 2001.

INS A₂ 8 FIELD OF THE INVENTION

9 The invention relates to a low conductivity thermal barrier
10 coating, in particular to a low conductivity thermal barrier
11 coating containing zirconia and/or hafnia, and a combination of
12 rare earth oxides and/or certain other oxides.

13
14 BACKGROUND OF THE INVENTION

15 Thermal barrier coatings are thin ceramic layers that are
16 used to insulate air-cooled metallic components from high
17 temperature gases in gas turbine or other heat engines. Such
18 coatings are useful in protecting and extending the service life
19 of metallic components exposed to high temperatures, such as jet
20 engine turbine blades. Thermal barrier coatings composed of
21 yttria-stabilized zirconia are known, wherein the yttria
22 typically makes up seven to nine weight percent (or four to five
23 molar percent) of the total composition. These coatings are
24 typically applied using plasma spraying or physical vapor
25 deposition process in which melted ceramic particles or
26 vaporized ceramic clouds are deposited onto the surface of the
27 component that is to be protected. Thermal barrier coatings are
28 somewhat porous with overall porosities generally in the range
29 of 5 to 20%. This porosity serves to reduce the coating's
30 thermal conductivity below the intrinsic conductivity of the

1 dense ceramic, as well as to improve the coating's strain
2 tolerance. However, the coating conductivity will increase as
3 the porosity decreases in high temperature service due to
4 ceramic sintering.

5
6 In a jet engine, higher operating temperatures lead to
7 greater efficiency. However, higher temperatures also cause
8 more problems such as higher stresses, increased materials phase
9 instability and thermal oxidation, leading to premature failure
10 of the component. A ceramic coating with lower thermal
11 conductivity and improved high temperature stability would allow
12 higher operating temperatures while preserving operating life of
13 the coated component. Accordingly there is a need for thermal
14 barrier coatings with a lower conductivity and better sintering
15 resistance than prior art coatings. Such a coating ideally
16 would retain low conductivity after many hours of high
17 temperature service. A laser test, recently developed by the
18 current inventors has allowed simultaneous testing of
19 durability, conductivity, and conductivity increase due to
20 sintering under turbine-level high heat flux conditions. Thus
21 the thermal barrier coating advances described in this invention
22 have had the benefit of this new test approach.

23 24 SUMMARY OF THE INVENTION

25 A thermal barrier coating composition is provided. The
26 composition is about 46-97 molar percent base oxide, about 2-25
27 molar percent primary stabilizer, about 0.5-12.5 molar percent
28 group A dopant, and about 0.5-12.5 molar percent group B dopant.
29 The base oxide is selected from the group consisting of ZrO_2 ,
30 HfO_2 , and combinations thereof. The primary stabilizer dopant is

1 selected from the group consisting of Y_2O_3 , Dy_2O_3 , and Er_2O_3 and
2 combinations thereof. The group A dopant is selected from the
3 group consisting of alkaline earth oxides, transition metal
4 oxides, rare earth oxides and combinations thereof. The group B
5 dopant is selected from the group consisting of Nd_2O_3 , Sm_2O_3 ,
6 Gd_2O_3 , Eu_2O_3 and combinations thereof.

7
8 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE
9 INVENTION

10 As used herein and in the claims, all percentages are given
11 as molar percent unless otherwise indicated. As used herein,
12 when a preferred range such as 5-25 is given, this means
13 preferably at least 5 and, separately and independently,
14 preferably not more than 25.

15
16 The thermal barrier coating of the present invention has
17 the following preferred formulation or table of components. In
18 this formulation or table of components, any preferred or less
19 preferred molar percent or molar percent range of any component
20 can be combined with any preferred or less preferred molar
21 percent or molar percent range of any of the other components;
22 it is not required or necessary that all or any of the molar
23 percents or molar percent ranges come from the same column.

T0050

TABLE OF COMPONENTS			
	MOLAR PERCENTS		
	Less Preferred	Less Preferred	Preferred
Base	60-93 46-97	82-91 73-92	86 84-89
Primary Stabilizer	4-17 3-20 2-25	6-12 4-14	9 7-10
Group A Dopant	0.9-8 0.8-9 0.7-10 0.5-12 0-25	1.75-4.5 1.5-5 1.25-6 1-7	2.5
Group B Dopant	0.9-8 0.8-9 0.7-10 0.5-12 0-25	1.75-4.5 1.5-5 1.25-6 1-7	2.5

The base oxide is preferably zirconium oxide (ZrO_2), hafnium oxide (HfO_2), or a combination of zirconium oxide and hafnium oxide.

The primary stabilizer is preferably yttrium oxide (Y_2O_3), less preferably dysprosium oxide (Dy_2O_3), less preferably erbium oxide (Er_2O_3) or combinations of any of these.

The group A dopant is preferably scandia oxide (Sc_2O_3) or ytterbium oxide (Yb_2O_3), less preferably combinations of these, less preferably nickel (II) oxide (NiO), chromium (III) oxide (Cr_2O_3), Cobalt (II) oxide CoO , iron (III) oxide (Fe_2O_3), magnesium (II) oxide (MgO), less preferably titanium (IV) oxide (TiO_2), ruthenium (IV) oxide (RuO_2), tantalum oxide (Ta_2O_5) or combinations of any of the foregoing, less preferably any other rare earth oxide, including or excluding erbium oxide (Er_2O_3), alkaline earth metal oxide, transition metal oxide, or

1 combinations of any of the foregoing.

2
3 The radii of cations of the group A dopant oxide preferably
4 are smaller than the radii of the cations of the primary
5 stabilizer and/or the base oxide.

6
7 The group B dopant is preferably neodymium oxide (Nd_2O_3) or
8 gadolinium oxide (Gd_2O_3), less preferably samarium oxide (Sm_2O_3),
9 less preferably europium oxide (Eu_2O_3), or combinations of any of
10 these.

11
12 The radii of cations of the group B dopant oxide preferably
13 are larger than the radii of the cations of the primary
14 stabilizer and/or the base oxide.

15
16 The group A and group B dopants are preferably present in
17 substantially equal molar percents in the thermal barrier
18 composition. Less preferably the group A and group B dopants
19 are present in a molar percent ratio between 1:1:1 to 1:1.1,
20 less preferably 1.5:1 to 1:1.5, less preferably 1:2 and 2:1,
21 less preferably 1:4 to 4:1, less preferably 1:8 to 8:1. Less
22 preferably the group A or group B dopant can be omitted
23 entirely.

24
25 The molar percent ratio between the primary stabilizer and
26 the total group A and group B dopants is preferably about 2:1 to
27 5:1, less preferably about 1.5:1 to 6:1, less preferably about
28 1:1 to 10:1.

1 Other additives known in the art may also be added in
2 conventional amounts. Because of the difficulty in separating
3 rare earth metals from each other, the listed percentages
4 indicate that the given component (base oxide, primary
5 stabilizer dopant, Group A dopant, Group B dopant) consists
6 essentially of the given metal oxide compound, with allowance
7 for impurities normally tolerated from commercially available
8 sources. The components of the composition are combined as
9 known in the art to form the coating composition.

10
11 The invented thermal barrier coating composition is
12 preferably used to coat metal surfaces subject to high
13 temperatures, such as turbine blades in jet engines. The
14 coating may be applied to the substrate in thicknesses and using
15 methods known in the art, principally either plasma spraying or
16 physical vapor deposition.

17
18 Without wishing to be bound by any particular theory, it is
19 believed that the invention operates under the following
20 theories.

21
22 As discussed above this innovation involves the addition of
23 group A and group B dopant oxides to the zirconia (hafnia)-
24 yttria or other zirconia (hafnia) based systems. The group A and
25 group B dopants are primarily intended to serve three functions:

26
27 (1) Creation of thermodynamically stable, highly defective
28 lattice structures with controlled ranges of defect cluster
29 sizes. The intent of these complex structures is to effectively
30 attenuate and scatter lattice phonon waves as well as radiative

1 photon waves at a wide spectrum of frequencies, thus
2 significantly reducing the oxide intrinsic lattice and radiation
3 thermal conductivity;

4
5 (2) Production of highly distorted lattice structures with
6 essentially immobile defect clusters and/or nanoscale ordered
7 phases which effectively reduce the mobile defect concentration
8 and suppress the atomic mobility and mass transport, thus
9 significantly improving the oxide sintering-creep resistance;

10
11 (3) Improvements in mechanical properties such as fracture
12 toughness as well as durability from the formation of complex
13 nanoscale defect clusters.

14
15 The composition design of the multiple component thermal
16 barrier coating systems is based on following considerations:

17
18 (1) Lattice elastic strain energy and ionic size considerations:

19 One or more pairs of additional dopants are incorporated in
20 the ZrO_2 (HfO_2)-based alloys. The cation ionic sizes of the group
21 A and group B dopants are preferably smaller and larger,
22 respectively, than that of the primary dopant or the base
23 oxides. This will effectively produce lattice distortion in the
24 ceramic alloy solid solutions and it will facilitate local ionic
25 segregation (defect clustering).

26
27 (2) Electroneutrality considerations

28 The one or more pairs of additional dopants incorporated in
29 the ZrO_2 (HfO_2) based oxides preferably have cation valencies
30 that are either less than that of zirconia (e.g., valency +2 or

1 +3) or larger than that of zirconia (i.e., valency greater than
2 +4), and less preferably equal to that of zirconia (i.e.,
3 valency +4) but with significantly different ionic radius than
4 zirconia. Therefore, high concentration of highly associated
5 defects will be created and stabilized based on the
6 electroneutrality conditions. Strong dopant-oxygen vacancy and
7 dopant-dopant interactions are expected which will promote the
8 formation of extended, immobile defect clusters.

9
10 (3) Oxide free energy formation, oxide stability and
11 polarization considerations

12 The one or more pairs of additional dopants incorporated in
13 the ZrO_2 (HfO_2) based oxide systems are preferably selected so as
14 to possess the highest possible (most negative value) free
15 energy of formation of the dopant oxides. High free energy of
16 formation of a dopant oxide represents high stability of the
17 oxide in an oxygen-containing atmosphere, which is greatly
18 desirable.

19
20 A high free energy of formation of a dopant oxide may also
21 correlate with high polarization of the oxide. The additions of
22 the dopant oxides with mixed polarization and ionic sizes may
23 further introduce lattice defect and distortion for reduced
24 thermal conductivity and improved sintering-creep resistance.

25
26 (4) Atomic weight and solubility considerations

27 High dopant atomic weight is beneficial for improving
28 lattice scattering. High dopant solubility is beneficial for
29 increasing dopant concentrations and thus defect concentrations.
30 A mixture of high- and low-solubility dopants and of high- and

low-atomic weight will promote complex structures and thus improved lattice scattering.

The following Examples further illustrate various aspects of the invention. Examples 1-4 each show the components of a preferred embodiment of the invention, the amounts of the ingredients, and the resulting thermal conductivity observed after 20-hour high temperature testing at about 1316°C (2400°F) in steady-state laser conductivity tests. The "Group A Overdopant" shown in Example 4 is an example of combining two different types of group A dopants, in this case resulting in a greater total molar percentage of group A dopant than group B dopant. Example 5 shows the baseline control sample, a standard yttria-stabilized zirconia. Percentages are given in molar percent, abbreviated as "mol%".

T0100

Example:	1	2	3	4	5
Base Oxide	Zirconia 94 mol%	Zirconia 86.5 mol%	Zirconia 86.5 mol%	Zirconia 71.25 mol%	Zirconia 95.5 mol%
Primary Stabilizer	Yttria 3 mol%	Yttria 9 mol%	Yttria 9 mol%	Yttria 14 mol%	Yttria 4.5 mol%
Group A dopant	Ytterbia 1.5 mol%	Ytterbia 2.25 mol%	Ytterbia 2.25 mol%	Ytterbia 7 mol%	0
Group B dopant	Samaria 1.5 mol%	Neodymia 2.25 mol%	Gadolinia 2.25 mol%	Neodymia 7 mol%	0
Group A Overdopant	0	0	0	Scandia 0.75 mol%	0
Thermal Conductivity (W/m-K)	0.72	0.63	0.70	0.56	1.35

1 As these results demonstrate, the addition of dopants
2 according to the present invention reduces the 20-hour thermal
3 conductivity of the coatings. The coating sintering resistance
4 at high temperature is also significantly improved, as suggested
5 by the significantly lowered rates of the conductivity increase.
6 The magnitude of increases in thermal conductivity after 20
7 hours in coatings according to the present invention were
8 generally approximately 25-50% less than the magnitude of
9 increase observed in similarly applied prior art 4.55 mol%
10 yttria stabilized zirconia coatings. The foregoing results were
11 surprising and unexpected.

12
13 Although the preferred embodiments of the invention have
14 been shown and described, it should be understood that various
15 modifications and changes may be resorted to without departing
16 from the scope of the invention as disclosed and claimed herein.